The Effect of Nitrogen-Containing Heterocyclic Compounds on the Electrode Process of Europium

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The reduction of Eu(III) to Eu(II) at d. m. e. proceeds irreversibly in the most of inorganic supporting electrolytes. Addition of small quantities of nitrogen-containing heterocyclic compounds such as 1, 10-phenanthroline (phen), 2, 2'-dipyridyl and acridine to the above solutions causes a shift of the half-wave potential to less negative values and makes the electrode process reversible. The resulted half-wave potentials are less negative than the standard oxidation-reduction potential of this redox system. Complex ion formation can be considered to cause a shift of reduction potentials to less negative values. However the complex ion formation of europium with phen in the bulk of the solution may not be accepted under the conditions in this investigation, because the shift of the half-wave potential can be observed at the ratio of europium to phen 10 to 1.

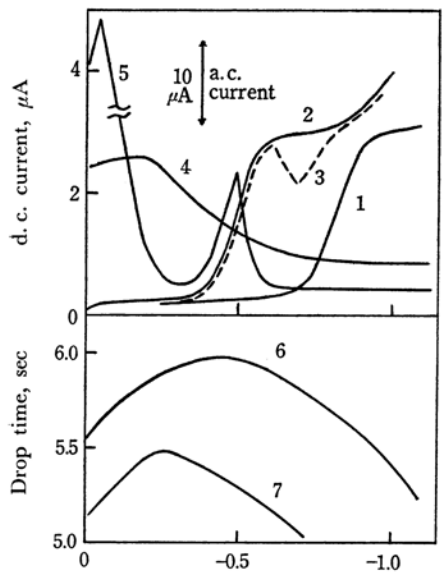

Fig. 1. The d. c. and the a. c. polarograms and the electrocapillary curves.
d. c. polarograms:
(1) 1 mM Eu^{3+} in 0.5 M Na_2SO_4; (2) (1)+1 mM phen, pH 6.4; (3) (1)+1 mM phen, pH 5.3
a. c. polarograms:
(4) the same as (1); (5) the same as (2)
electrocapillary curves:
(6) 0.5 M Na_2SO_4; (7) (6)+1 mM phen, pH 6.4

As seen in Fig. 1, the a. c. polarogram in the presence of phen shows two peaks, of which the first[1] (at less negative potential) can be attributed to the adsorption-desorption process of phen and the second to the reduction of Eu(III) to Eu(II). The a. c. base-current in the presence of phen is depressed comparing to that in the absence of phen in the potential region more negative than the first summit potential. Upon the addition of phen the electrocapillary curve of 0.5 M sodium sulfate solution is depressed on the both branches of the e. c. m. and the point of e. c. m. is shifted to less negative potential. From above observations it may be concluded that neutral phen molecules are strongly adsorbed on d. m. e. on the both branches of the e. c. m. and the point of e. c. m. is shifted to less negative potential, which makes europium cations approach easily to the electrode surface at less negative potentials and thus accelerates the rate of the reduction process. On the other hand, a minimum of the current-potential curve in the presence of phen at pH less than 5.5 appears in the potential region immediately after the limiting current is reached, which could be ascribed to the deceleration of the reduction process caused by the adsorption of a substance related to the phenanthrolium ions ($Hphen^+$).

Although the presence of surface active substances (SAS) usually cuases a deceleration of the rate of the reduction process,[2] a few cases have been found in which it shows a dual effect (acceleration and deceleration) on the rate of the reduction process.[3-5] The system being studied, therefore, might be regarded as a new case in which SAS exhibits a dual effect on the rate of the reduction process. However, this system is of specific and the mechanism of the deceleration process is different from those reported previously.

1) This peak splits into two at the lower concentration of neutral phen molecules.
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4) N. Tanaka and Y. Kikuchi, This Bulletin, **36**, 759 (1963).
5) F. Fujinaga and S. Okazaki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 600 (1964).